THIN FILM HYDROPHILIC COATINGS

BACKGROUND OF THE INVENTION:

The hydrophilicity of a solid surface can be an advantage in various situations:

1. Hydrophilic surfaces resist soiling by lipophilic substances such as oils, greases, fuels, spray-paints and waxes.
2. Hydrophilic surfaces often resist the absorption or adhesion of proteins, cells and related biological substances such as incrustations, thrombi or clusters of cells such as platelets.
3. Hydrophilic surfaces often resist fogging; this is an advantage for optical devices such as mirrors, windows, goggles or lenses.
4. Hydrophilic surfaces are often slippery in the presence of water. This can be utilized in bearings, surgical gloves, guide-wires or catheters.
5. Hydrophilic surfaces often show an improved capability to absorb and retain disinfectants, inks or dyes.

These examples suggest a number of practical applications or products benefiting from hydrophilic surfaces: medical devices, surgical gloves, bearings, lenses, mirrors, packaging means, pipes and valves, and many other products.

Most of the materials used for engineering, packaging or biomedical products are generally hydrophobic to various degrees. For instance, many plastics, rubbers and metal alloys are poorly wettable by water. Even glass and ceramics can benefit from a treatment which would render their surface highly wettable, or even swellable in water and/or slippery in the water-wetted state.

There are several methods used to increase the surface hydrophilicity of otherwise hydrophobic materials. For instance, hydrogels are sometimes used to construct an article with improved surface hydrophilicity. This approach has several disadvantages:

First, the swelling of the hydrogel in water, or its deswelling or drying, changes its size, shape and mechanical properties. This may be a considerable complication in a number of instances.

Also, not all hydrogel surfaces are truly hydrophilic or even slippery. It is sometimes necessary to chemically treat the hydrogel articles to introduce ionically charged groups which increase surface hydrophilicity and leave a slippery surface, as it is described in U.S. Pat. No. 4,810,543 by Gould and Kliment, in U.S. Pat. No. 4,183,884 by Wichterle and Stoy, in U.S. Pat. No. 5,217,026 by G. Stoy and V. Stoy or in U.S. Pat. No. 4,026,296 by Stoy, et al. This so called "superhydrophilization" is an additional process step which can considerably complicate the manufacture and use of the final product. It is particularly difficult to create the superhydrophilic surface on very thin hydrogel articles or layers.

Similar methods of surface hydrophilization via chemical treatment can also be applied to some hydrophobic plastics. For instance, the surfaces of poly(acrylamides), poly(methacrylates) and poly(acrylates) can be superhydrophilized by hydrolysis or by reesterification combined with sulfation, as described in U.S. Pat. No. 3,895,169 by Wichterle or in U.S. Pat. No. 4,921,497 by Sulc and Krcova, etc. Plastics containing nitrile groups can be surface-hydrolyzed or aminolyzed as described in the U.S. Pat. No. 4,943,618 by V. Stoy, G. Stoy and Lovy and in U.S. Pat. No. 5,252,692 by Lovy and Stoy.

Hydrophobic polyolefines, such as polyethylene or polypropylene, can be surface-hydrophilized by oxidation, amination or sulfonation by either gaseous or liquid reagents or by other well known methods. The surface is sometimes activated by suitable means such as corona discharge.

Another variant of surface hydrophilization is the grafting of hydrophilic monomers initiated by irradiation or chemical activation of the hydrophobic surface. Such methods are described, for instance, in U.S. Pat. No. 3,826,678, European Patent Application No. 82850200.5, U.S. Pat. No. 4,377,010, U.S. Pat. No. 4,387,183 and U.S. Pat. No. 4,291,133. These surface-modification methods rarely yield a truly hydrophilic, slippery surface. In most cases, it results in increased wettability which, for example, is required for printing and adhesive bonding. Another desired result is improved blood compatibility. These methods are limited to surfaces which are suitably reactive; they can be rarely applied to surfaces such as metals or glass.

Another common hydrophilization method consists in the application of hydrophilic (or hydrogel) coatings. Hydrophilic polyurethanes are often considered the most suitable class of polymers for hydrogel coatings because of their relative flexibility in the dry state, solubility in several kinds of the volatile solvents and reactivity allowing crosslinking or anchoring reactions. Many hydrophilic polyurethanes are described in patent literature (see e.g. U.S. Pat. Nos. 3,822,238; 3,975,350; 4,156,066; 4,156,067; 4,255,550; 4,359,558; 4,920,172; 4,789,720; 4,810,543; 4,743,673; 4,798,876; 4,490,423; 4,454,309; 4,451,635; 4,439,583; 4,255,550), and many of them were suggested as a basis for hydrophilic coatings of catheters and other articles. Another frequently used polymer system is based on poly(2-hydroxyethylmethacrylate), or poly(HEMA). Such coatings are described in, for instance, U.S. Pat. No. 4,527,293; U.S. Pat. No. 3,861,396 and U.S. Pat. No. 3,566,874.

The main problem of the coating approach is that proper adhesion of the coating to the substrate requires a certain similarity between the two (i.e. a certain hydrophobicity). This conflicts with the requirement of the high surface hydration of the coating.

The problem of adhesion increases with the coating hydrophilicity for several reasons:

1. Coatings with high hydrophilicity undergo substantial volume changes during hydration and drying. These changes create stress on the interface which often leads to delamination or peeling.
2. Highly hydrophilic coatings are primarily composed of polymers with highly polar groups which are hydrated in the presence of water. While hydrated, these groups cannot enhance the adhesion between the surfaces.
3. The large difference in wetting characteristics implies a large difference in the cohesion energies of both materials, and thus a high interfacial free energy in the bonded state. Such a configuration poses a basic thermodynamical instability.
4. Highly hydrophilic polymers are often rigid or even brittle in the dry state. Their rigidity leads to cracking, peeling and flaking off the substrate.

This inherent problem can be solved by a combination of several methods of various technical complexity. The methods most frequently used are the following ones:

1. The hydrophilic layer can be "anchored" to the substrate by chemical bonds reaching across the interface. This bonding has to be carried out in such a way that it does not affect the surface hydrophilicity. Such reactive hydrophilic coatings are described in European Patent No. 00993093B1 and British Patent No. 1,600,963. Micklus et al. therein describe hydrophilic coat-